& Andreetti, 1983; Courtois *et al.*, 1986; Suwińska & Lipkowski, 1988). The conformation of the macrocyclic ring is described by torsion angles (Table 3). The sequence of dihedral angles along the macrocylic ring is $g^+ag^-g^-ag^-aa0aag^+aag^-g^+g^-g^-$ and is different from that for the complex of α-D-mannosido-benzo-18-crown-6 (II) with KSCN (Suwińska & Lipkowski, 1988) which was much closer to the 'ideal' conformation with energetically preferred *gauche* (*g*) conformation about C—C bonds and anti (*a*) about C—O bonds. The *gauche* conformation about C(11)—O(15), C(17)—O(18), C(37)—O(38) and C(12)—O(38) bonds forces the macrocyclic ring into a highly distorted conformation, minimizing the size of the molecular cavity. The cavity, which in complexed form contains the K^+ cation, in the present structure contains H atoms H(11) and H(16*a*) which are pointing towards the center of the macrocyclic cavity, giving short intramolecular contacts 'across' the ring (Fig. 2). The O(21) and O(32) atoms are out of the plane of the naphthalene rings by −0·082 (2) and +0·183 (2) Å, respectively. The four O atoms of the macrocyclic ring, O(18), O(21), O(32) and O(35), are coplanar to within 0·022 (2) Å; the remaining two O atoms deviate from that plane by −1·299 (2) Å [O(15)] and −1·019 (2) Å [O(38)].

The shortest interatomic distances between non-H atoms of adjacent different molecules are: no C···C or O···O below 3·5 Å, O···C 3·389 (4) Å between O(4) and C(30) at $1-x, \frac{1}{2}+y, 2-z$.

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1-Phosphabicyclo[3.3.0]octane 1-Sulfide

By U. Baumeister*

Department of Crystallography, A. Mickiewicz University, ul. Grunwaldska 6, 60–780 *Poznań, Poland*

and H. Hartung† and F. Krech

Sektion Chemie, Martin-Luther-Universität Halle-Wittenberg, Postfach, Halle, DDR-4010,
German Democratic Republic

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Abstract. $C_7H_{13}PS$, $M_r = 160{\cdot}2$, monoclinic, $P2_1/c$, $a = 7{\cdot}647\ (1)$, $b = 7{\cdot}841\ (1)$, $c = 14{\cdot}508\ (4)$ Å, $\beta = 99{\cdot}96\ (3)°$, $V = 856{\cdot}8\ (3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}24$ Mg m^{-3}, $\lambda(\text{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 4{\cdot}43$ mm^{-1}, $F(000) = 344$, $T = 291$ K, final $R = 0{\cdot}056$ for 981 observed reflections. The phospholane rings of the 1-phosphabicyclo[3.3.0]octane 1-sulfide molecule are *cis*-fused and both adopt an envelope conformation. In one ring the flap C atom is positionally disordered. As a result of this disorder, the title compound exists in both an *exo–endo* conformation (main occupancy) and an *endo–endo* conformation in the solid state.

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* Permanent address: Sektion Chemie, Martin-Luther-Universität Halle-Wittenberg, Postfach, Halle, DDR-4010.

† To whom correspondence should be addressed.

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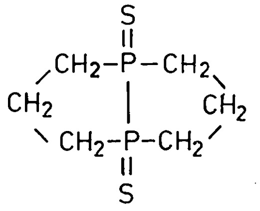
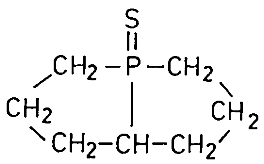
Introduction. As a result of theoretical and experimental investigations, the chair–chair conformation (*CC*) has been proved to be the preferred one for unsubstituted carbabicyclo[3.3.1]nonane. However, the boat–chair (*BC*) and boat–boat (*BB*) conformations can be stabilized by appropriate substitution of or at the C atoms by heteroatoms or bulky substituents, respectively. Recently, we were able to show that the phospha-substituted compounds 1-phosphabicyclo[3.3.1]nonane 1-sulfide (Baumeister, Hartung & Krech, 1988) and 1,5-diphosphabicyclo[3.3.1]nonane 1,5-disulfide (Hartung, Baumeister, Rauch & Krech, 1988) adopt *CC* conformations in the solid state. Similar conclusions arise from a consideration of the possible conformations of the bicyclo[3.3.0]octane system. For its *cis*-conformation analogous to *CC*, *BC* and *BB*, three flap isomers with *endo–endo*, *exo–endo* and *exo–exo* conformations have to be considered.



(1)



(2)

As a result of our earlier X-ray studies the molecules of 1,5-diphosphabicyclo[3.3.0]octane 1,5-disulfide (1) have been proved to be in an *endo–endo* conformation with C_{2v} symmetry (Kaiser, Richter & Hartung, 1978; Hartung, Hickel, Kaiser & Richter, 1979). That compound is dimorphic and its two modifications do not differ significantly in molecular structure but only in crystal packing (packing polymorphism). We now present the results of an X-ray analysis of the closely related compound 1-phosphabicyclo[3.3.0]octane 1-sulfide (2) in which only one bridgehead position is occupied by a P atom.

Experimental. The title compound (2) was first synthesized by Krech (1978). A colorless clear crystal obtained by recrystallization from hexane with dimensions 0·08 × 0·24 × 0·28 mm was investigated on a Syntex $P2_1$ diffractometer using graphite-monochromated Cu $K\alpha$ radiation. Lattice parameters were derived from least-squares refinement of the setting angles of 15 reflections. Intensity data measurements: θ–2θ scan; $2\theta_{\max} = 115°$; h,k,l range from $-8,0,0$ to $8,8,15$; 1127 unique reflections, 984 with $I \geq 1·96\sigma(I)$ considered observed. After the 24 h of data collection process the intensities of check reflections had decreased by 24·2% for 022 and 28·8% for $\bar{2}12$ of their starting values. The decrease was obviously due to slight decomposition and appeared to be linear, therefore a 'linear-decay' correction was applied. Lp corrections were carried out but absorption effects were ignored. The structure was solved by the direct-method routine of *SHELXS*86 (Sheldrick, 1986) and refined on F by full-matrix least squares with anisotropic displacement parameters for the non-H atoms. H atoms were included in the model at calculated positions (C—H = 1·08 Å) and were 'riding' on the corresponding C atoms during the refinement. After omitting three reflections with large $\Delta F/\sigma(F)$, R was 0·058. At this stage the displacement parameters of atom C(2) were significantly higher than those of the other C atoms. Moreover, a difference Fourier map revealed a peak at a position also geometrically allowed for C(2) with respect to its neighbors C(1) and C(3). Consequently, a disorder of C(2) was assumed with two alternative positions of this atom (hereafter referred to as *A* and *B*). The refinement was continued with two positions for C(2) and H(11)···H(32) (Fig. 1) and an individual isotropic displacement parameter and geometric constraints (C—C = 1·54 Å, C—C—C = 112°) for C(2*B*). The sum of the site-occupation factors over the alternative conformations was unity and their values have been refined to 0·83 (2) and 0·17 (2) for *A* and *B*, respectively. The final weighting scheme was $w^{-1} = \sigma^2(F) + 6·15 \times 10^{-4}F^2$, an empirical extinction correction was performed with $F_{\rm corr} = F_c(1 - 10^{-6}\chi F_c^2/\sin\theta)$ where χ refined to 3·6 (3). The final R was 0·056 ($wR = 0·066$). Further details of refinement: 11·1 reflections/parameter; in final cycle $\Delta/\sigma \leq 0·013$; max. and min. heights in final difference Fourier synthesis 0·50 and $-0·28$ e Å^{-3}, respectively; atomic scattering factors from *SHELX*. Calculations were performed on an IBM-PC using programs *XTL* (Syntex, 1973), *SHELX*76 (Sheldrick, 1976) and *SHELXS*86 (Sheldrick, 1986).

Discussion. Final fractional coordinates and equivalent isotropic displacement parameters are listed in Table 1.[*] The essential structural and conformational features of the 1-phosphabicyclo[3.3.0]octane 1-sulfide molecule are given in Figs. 1 and 2 and in Table 2. The phospholane rings I [C(1)...] and II [C(4)...] are *cis*-fused [common atoms P and C(7)] and both adopt envelope conformations with C(2) and C(5) as flaps. As already discussed, the structure of (2) is disordered in such a way that atom C(2) of

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[*] Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52392 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters and equivalent isotropic displacement parameters* (Å^2) *of non*-H *atoms with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S	0·7992 (2)	−0·1944 (2)	0·60807 (8)	0·0625 (5)
P	0·8034 (2)	0·0492 (2)	0·63799 (6)	0·0440 (4)
C(1)	0·7255 (6)	0·1030 (6)	0·7463 (3)	0·060 (2)
C(2*A*)	0·5330 (9)	0·1680 (10)	0·7071 (5)	0·074 (3)
C(2*B*)	0·638 (7)	0·279 (3)	0·725 (2)	0·12 (2)*
C(3)	0·5412 (7)	0·2858 (7)	0·6230 (4)	0·075 (2)
C(4)	0·7868 (7)	0·3162 (7)	0·5218 (4)	0·068 (2)
C(5)	0·9520 (7)	0·3387 (7)	0·5984 (4)	0·070 (2)
C(6)	1·0093 (6)	0·1620 (7)	0·6330 (3)	0·059 (2)
C(7)	0·6584 (6)	0·1966 (6)	0·5619 (3)	0·053 (2)

* Isotropic displacement parameter.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

P—S	1·957 (2)	C(3)—C(2*A*)	1·540 (9)
P—C(1)	1·823 (5)	C(3)—C(2*B*)	1·541 (22)
P—C(6)	1·818 (5)	C(3)—C(7)	1·535 (7)
P—C(7)	1·833 (5)	C(4)—C(7)	1·543 (7)
C(1)—C(2*A*)	1·569 (8)	C(4)—C(5)	1·541 (7)
C(1)—C(2*B*)	1·541 (27)	C(5)—C(6)	1·513 (8)
S—P—C(1)	114·9 (2)	C(1)—C(2*B*)—C(3)	109·9 (1·3)
S—P—C(6)	116·5 (2)	C(2*A*)—C(3)—C(7)	107·0 (5)
S—P—C(7)	119·8 (2)	C(2*B*)—C(3)—C(7)	108·1 (1.2)
C(1)—P—C(6)	109·6 (3)	C(5)—C(4)—C(7)	107·1 (4)
C(1)—P—C(7)	96·9 (2)	C(4)—C(5)—C(6)	106·8 (4)
C(6)—P—C(7)	96·2 (2)	P—C(6)—C(5)	104·8 (4)
P—C(1)—C(2*A*)	100·9 (4)	C(3)—C(7)—C(4)	114·5 (4)
P—C(1)—C(2*B*)	103·5 (7)	P—C(7)—C(3)	107·0 (3)
C(1)—C(2*A*)—C(3)	108·5 (5)	P—C(7)—C(4)	104·6 (4)

ring I can occupy two alternative positions *A* and *B* with site-occupation ratio of about 5:1. The main component has an *exo–endo* conformation with C(2*A*) turned towards and C(5) turned away from the S atom whereas the by-component adopts an *endo–endo* conformation. This result is a rather surprising one considering the sole appearance of the *endo–endo* conformation in both crystalline modifications of (1). It should be mentioned here that a variable-temperature NMR study revealed the existence of only one conformer of (2) in solution. As can be seen from Fig. 2, the deviation from ideal envelope geometry is rather different for the three phospholane rings. The distortion is nearly insignificant for rings I*A* and I*B* but fairly marked for ring II. All atoms defining the best least-squares plane through P, C(1), C(3), C(7) (plane 1) are coplanar within experimental error whereas the three C atoms of plane 2 [through P, C(4), C(6), C(7)] deviate to some extent [about ±0·080 (5) Å] from this plane. The angle between planes 1 and 2 is 113·4 (2)° and is nearly the same as 112·0° in 1-phosphabicyclo[3.3.1]-nonane 1-sulfide (Baumeister, Hartung & Krech, 1988). The observed bond lengths and angles agree well with corresponding values in the literature, in particular with those in the three above-mentioned closely related phosphabicycloalkane sulfides. The coordination around the P atom is that of a slightly distorted tetrahedron. The C—P—S bond angles are all increased from tetrahedral [mean 117·1 (20)°] whereas the C—P—C angles are ideal or decreased [mean 100·9 (62)°]. The molecular packing is shown in Fig. 3. No intermolecular contact is significantly shorter than the sum of the appropriate van der Waals radii. Because this is true for both conforma-

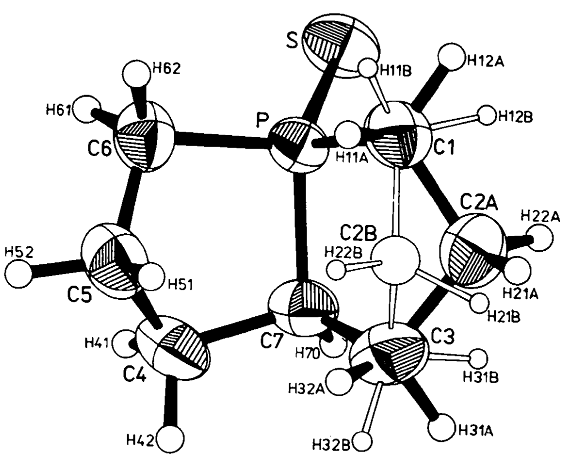

Fig. 1. *ORTEP* plot (Johnson, 1976) of the molecular structure of (2) showing atom labels and disordering of phospholane ring I [thermal ellipsoids at the 50% probability level, arbitrary size of atom C(2*B*) and H atoms].

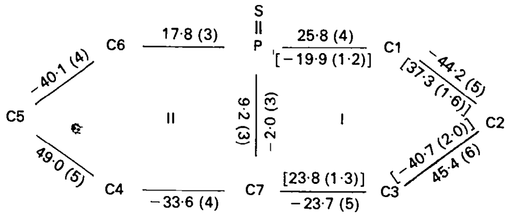

Fig. 2. Endocyclic torsion angles (°) of the phospholane rings in (2). Values in square brackets refer to position *B* of the disordered atom C(2).

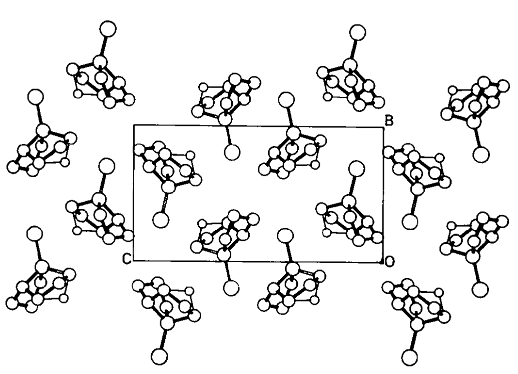

Fig. 3. *PLUTO* plot (Motherwell, 1978) of the crystal structure.

tions, there are no simple crystal-packing arguments for the observed preference of the *exo–endo* conformation.

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A Charge-Transfer Complex of Benzene with a Highly Twisted Perylene Derivative

By Mahin Sadrai,* George R. Bird, Joseph A. Potenza and Harvey J. Schugar

Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903, *USA*

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Abstract. $2C_6H_6.C_{26}H_6Cl_8N_2O_4$, benzene–1,2,5,6,7,8,11,12-octachloro-*N*,*N*′-dimethylperylene-3,4:9,10-bis(dicarboximide) (Cl_8DMP) (2/1), $M_r = 850·20$, orthorhombic, $Pna2_1$, $a = 23·076$ (2), $b = 7·2492$ (6), $c = 20·277$ (2) Å, $V = 3392·0$ (8) Å^3, $Z = 4$, $D_m = 1·69$ (1), $D_x = 1·665$ g cm^{-3}, μ(Mo $K\alpha$, $\lambda = 0·71073$ Å) = 7·1 cm^{-1}, $F(000) = 1712$, $T = 297$ (1) K, $R_F = 0·061$ for 2134 observed reflections. The structure contains alternating benzene and Cl_8DMP molecules stacked along **b** to form a 2:1 donor–acceptor complex. The Cl_8DMP molecule is highly twisted as a result of short intramolecular bay Cl···Cl contacts [3·109 (3), 3·136 (3) Å]. The central ring of the perylene fragment is substantially distorted from planarity; internal torsion angles range from 16 (1) to 32 (1)°.

Introduction. The highly chlorinated derivative of perylene, Cl_8DMP, was prepared as part of an effort to synthesize and examine a series of electron acceptors as candidates for incorporation in solar photovoltaic cells (Panayotatos, Parikh, Sauers, Bird, Piechowski & Husain, 1986) designed to work in the *p–n* mode with a compatible pair of stable solid organic dyes. The unchlorinated perylene diimide is a well known commercial dye and an efficient photoconductor (Popovic, Loutfy & Hor, 1985), but lacks strong electron affinity. It is also an exceedingly insoluble seven-ring aromatic molecule. Cl_8DMP has greater electron affinity and is soluble in a variety of organic solvents. Crystallization from a solution of Cl_8DMP in benzene yielded a 2:1 benzene–Cl_8DMP complex whose structure we report here.

Experimental. Cl_8DMP was prepared by reacting commercially obtained *N*,*N*′-dimethylperylene-3,4:9,10-bis(dicarboximide) at 333 K with chlorosulfonic acid and excess chlorine; iodine was used as a catalyst. Mass-spectral analysis of the reaction product indicated the presence of hexachloro, heptachloro, and octachloro derivatives which were separated by column chromatography (silica-gel column, benzene eluent). Diffraction-quality crystals were grown by evaporation from benzene.

Structure solution: D_m by flotation; dark-red prism 0·25 × 0·35 × 0·45 mm; Enraf–Nonius CAD-4 diffractometer; graphite-monochromated Mo $K\alpha$ radiation; θ–2θ scan. Reciprocal-lattice symmetry and systematic absences ($0kl$, $k + l = 2n + 1$; $h0l$, $h = 2n + 1$) consistent with space group $Pna2_1$. Cell constants from setting angles of 25 reflections with $13·40 < \theta < 18·26°$; data corrected for Lorentz, polarization and absorption (empirical correction, ψ scan; $0·95 < T < 1·00$) effects. Variation in intensity

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* Present address: Department of Technology, St. Cloud State University, St. Cloud, MN, USA.

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